

Electronic structure of the $c(4 \times 2)$ reconstructed Ge(001) surface

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We investigate the electronic structure of the $c(4 \times 2)$ reconstructed Ge(001) surface using band structure calculations based on density functional theory and the generalized gradient approximation. In particular, we take into account the details of surface reconstruction by means of well relaxed crystal structures. The surface electronic states are identified and the local density of states is compared to recent data from scanning tunneling spectroscopy. We obtain almost perfect agreement between theory and experiment for both the occupied and unoccupied states, which allows us to clarify the interpretation of the experimental data.

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The electronic properties of semiconductor surfaces attract great attention since these materials are of special interest for technological applications. Amongst all, the reconstruction of the Si(001) and Ge(001) surface has been studied most extensively. For the latter, the surface electronic structure recently has been investigated by scanning tunneling spectroscopy [1]. The experiments show a distinctly structured local density of states (DOS) close to the Fermi energy, associated with various surface states, see also [2, 3, 4]. Detailed knowledge about these surface states is highly desirable in order to understand self-organization of ad-atoms on the Ge(001) surface.

Various effects of self-organization have been reported for both Si and Ge surfaces. For example, self-assembled metallic chains are formed by In atoms on Si(111) [5] and Au atoms on Si(553) [6]. Electron motion in Ag films grown on the one-dimensional In chains is restricted to the chain direction, giving rise to quasi one-dimensional quantized Ag states [7]. Ultrathin films of Ag on Ge(111) are found to be strongly influenced by hybridization between the Ag and Ge surface states [8]. For the Ge(001) surface, Au growth comes along with a large variety of ordering phenomena as a function of both coverage and growth temperature [9]. Adsorption of Pt atoms instead of Au leads to well-ordered nanowire arrays after high-temperature annealing [10]. These spontaneously formed chains are thermodynamically stable, literally defect and kink free, and have lengths up to hundreds of nanometers. However, the conduction bands of the Pt chains seem to be strongly modified by the interaction with the Ge substrate [11]. Furthermore, as the Pt chains provide a confining potential, quantum mechanical interference between the Ge(001) surface electrons within the self-organized Pt arrays results in one-dimensional Ge states with energies resembling the energy levels of a quantum particle in a well [12].

The reconstruction of the Ge(001) surface has been investigated extensively from both the experimental and the theoretical point of view [13]. In particular, neighbouring surface atoms form asymmetric dimers on top of a slightly relaxed substrate, saturating one dangling bond per surface atom, see figure 1. Because the dimers

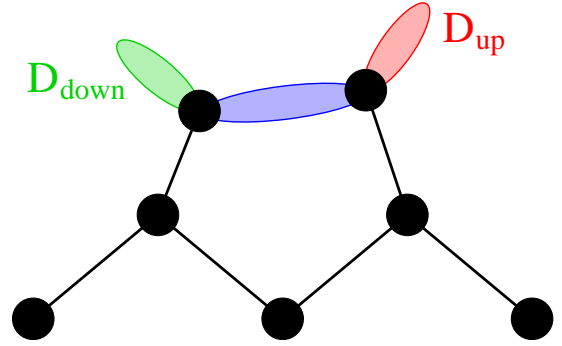


FIG. 1: (Schematic side-view of a buckled Ge surface dimer with dangling D_{down} and D_{up} bonds. The dimer bond tilts slightly out of the surface plane.

line up along the $\langle 110 \rangle$ direction, the Ge(001) surface is well characterized in terms of dimer rows. Further stabilization of the surface is reached by a distinct buckling of the dimers, giving rise to specific reconstruction patterns with respect to the realized buckling directions. The room temperature $p(2 \times 1)$ structure turns into a $c(4 \times 2)$ structure at low temperatures by means of an order-disorder phase transition, accompanied by a surface metal-insulator transition.

Early energy minimization calculations for the reconstructed Si(001) surface have been performed by Chadi [14], resulting in the characteristic dimer geometry as introduced for Ge(001) in the previous paragraph. Self-consistent electronic structure calculations for both the Si(001) and Ge(001) surface, using a combination of scattering theory and the local density functional formalism, have been reported by Krüger *et al.* [15], see also [16]. A comparative study of the surface reconstructions of diamond, Si, and Ge has been given by Krüger and Pollmann [17], including a comprehensive review on previous *ab initio* calculations. While for diamond a symmetric dimer configuration is established, asymmetric ordering leads to an energy gain of about 0.1 eV per dimer in the case of Si and Ge. The dimer formation on adsorption of In on Ge(001) has been analyzed by Çakmak and Srivastava

[18] via first principles total energy calculations. Their findings stress the importance of the details of the surface electronic structure for the adsorption mechanism. Expectedly, the same is true for the adsorption of other atoms or molecules, as alkali metals [19] or GeH_4 [20], for instance.

Experimental data by Gurlu, Zandvliet, and Poelsema [1] indicate that the very details of the surface reconstruction have serious effects on the $\text{Ge}(001)$ surface states. Well relaxed surfaces therefore are a necessary prerequisite for an adequate theoretical treatment of the surface electronic structure, which is the aim of the present paper. To be specific, we calculate the local \mathbf{k} -integrated DOS for the surface atoms in order to identify the surface states. Symmetry analysis then allows us to interrelate these states with particular bonds of the surface dimers, and to explain the electronic structure data obtained by Gurlu, Zandvliet, and Poelsema via scanning tunneling spectroscopy [1]. Previous theoretical studies failed to resolve the fine structure of the surface DOS.

Our first principles calculations rely on a supercell of the cubic Ge unit cell comprising one $c(4 \times 2)$ reconstructed surface array and extending two cubic unit cells perpendicular to the surface. With respect to the parent diamond lattice, our tetragonal supercell thus is given by the lattice vectors $(4, -4, 0)$, $(2, 2, 0)$, and $(0, 0, 2)$. As a consequence, it contains 64 Ge sites in 24 crystallographically inequivalent classes. For the structural optimization and the calculation of the electronic band structure, we apply the generalized gradient approximation within density functional theory, as implemented in the WIEN2k program package [21]. This is a famous full-potential linearized augmented plane wave code, having shown great capability in dealing with structural relaxation at surfaces and interfaces [22]. The x-ray diffraction data of Ferrer *et al.* [23] and the first principles data of Yoshimoto *et al.* [24] give rise to a reasonable starting point for the structural optimization. Convergence of the relaxation is assumed when the surface forces have decayed. To obtain reliable results, the charge density is represented by some 230,000 plane waves in our calculations and a \mathbf{k} -mesh with 40 points in the irreducible wedge of the Brillouin zone is applied. While Ge $3d$ orbitals are treated as semi-core states, the valence states consist of Ge $4s$ and $4p$ orbitals. We have checked our band structure data for convergence with respect to the thickness of the Ge slab. In particular, the interior of the slab resembles the bulk Ge DOS.

Figure 2 shows the local \mathbf{k} -integrated Ge DOS as resulting from our band structure calculations, for three characteristic atomic sites. The gross features agree well with recent findings of Stankiewicz and Jurczyszyn [25]. Panels (a) and (b) of figure 2 refer to the upper and lower dimer site, respectively. While the upper dimer site is shifted off the surface due to the buckling of the surface dimer, the lower dimer site approaches the surface. For comparison, panel (c) displays the local Ge DOS for an off-surface site in the third Ge layer. All three curves in

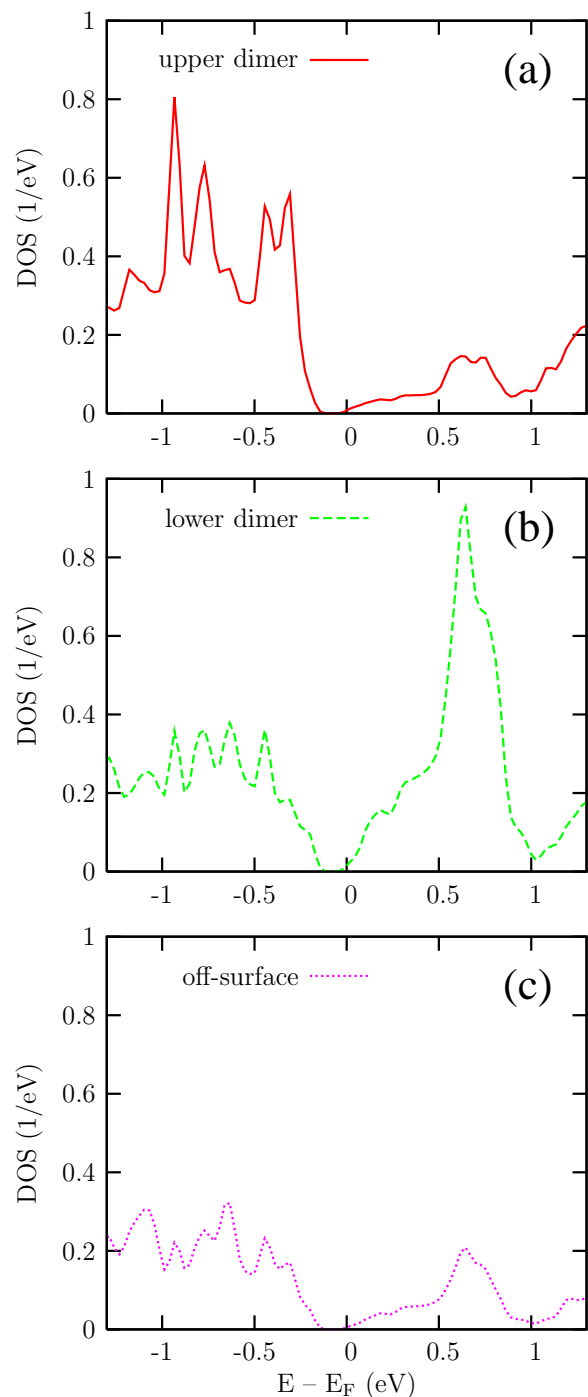


FIG. 2: Local Ge DOS for (a) the upper dimer site, (b) the lower dimer site, and (c) an off-surface site.

figure 2 show distinct densities of states both below and above the Fermi energy. The two regions are separated by an energy gap of about 0.15 eV, which is considerably less than the experimental gap of 0.7 eV for bulk Ge. It is likewise less than the values measured for the $\text{Ge}(001)$ surface, amounting to 0.3 – 0.9 eV [1, 26]. A discrepancy between the experimental and theoretical band gap is a

well-known phenomenon, tracing back to the approximations entering the band calculation. It has to be taken into account when DOS curves are compared, but does not affect our further conclusions.

To prepare for the analysis of the band structure data, we first address the surface states expected for the realized reconstruction pattern. Due to the dimer formation, σ -type bonding and antibonding bands should be formed. In addition, each Ge atom is left with one free dangling bond. For the buckled dimer, the dangling bond of the upward buckled atom gives rise to the D_{up} surface band, whereas the dangling bond of the downward buckled atom forms the D_{down} band. Due to charge transfer from the lower to the upper dimer site, the energy should be higher for the D_{down} than for the D_{up} state [13].

Comparing the Ge DOS for the upper and lower dimer site, see panels (a) and (b) of figure 2, we find contributions due to the atomic orbitals of the upper atom mainly below the Fermi energy. In contrast, states tracing back to the lower atom dominate above the Fermi energy. We first address the minority contributions to both the occupied and unoccupied states by relating them to the DOS of the off-surface Ge site given in figure 2 (c). We observe almost perfect agreement, even quantitatively, of the lower dimer site DOS and the off-surface DOS at energies below the Fermi level. The same is true for the upper dimer site DOS and the off-surface DOS at energies above the Fermi level. We therefore conclude that the minority contributions to the occupied and unoccupied bands result from bulk-like states, and are not characteristic for the Ge surface. Surface states lead to additional spectral weight, as observed for the upper/lower dimer site below/above the Fermi energy.

For the upper dimer site, the occupied states show a six peak structure in figure 2 (a), which likewise is visible for the lower dimer site in panel (b) and the off-surface site in panel (c). Peaks one (at -1.2 eV) and four (shoulder at -0.7 eV) are related to bulk-like states, as revealed by the off-surface DOS. Surface states correspondingly are located at about -0.9 eV, -0.8 eV, -0.4 eV, and -0.3 eV. For analyzing the unoccupied states, we turn to the lower dimer site in figure 2 (b), showing a pronounced peak in the energy range from the Fermi level up to 1 eV. However, on closer inspection this peak again consists of four surface states, located near 0.2 eV, 0.4 eV, 0.6 eV, and 0.7 eV. While the third state dominates the lower valence band, the other states contribute less spectral weight, therefore giving rise to distinct shoulders.

Next we investigate the origin of the various surface states. For this purpose, we decompose the Ge $4p$ DOS into its symmetry components. Contributions of p_y and p_z symmetry are found to be negligible in the vicinity of the Fermi energy, but almost all states have p_x symmetry. Since the surface plane is the yz -plane in our coordinates, this implies that an orientation perpendicular to the surface is typical for all Ge surface states. Corresponding $4p_x$ DOS curves are given in figure 3 for the upper as well as the lower dimer site. There are only two surface

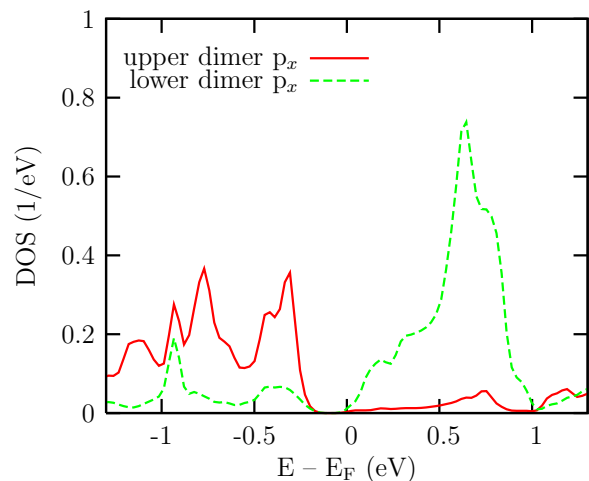


FIG. 3: Local Ge $4p_x$ DOS for the upper (solid line) and lower (dashed line) dimer site. The x -axis is oriented perpendicular to the surface.

states revealing significant contributions from both dimer atoms: the energetically lowest state at -0.9 eV and the energetically highest state at 0.7 eV. As a consequence, we attribute these peaks to the σ -type bonding and antibonding dimer bands, in correspondence with previous theoretical findings [16]. The remaining six surface states purely belong to either the upper or the lower dimer site. Therefore, the higher occupied and lower unoccupied surface states are clearly due to the dangling bonds of the upward and downward buckled Ge atom, respectively.

Turning to the comparison with the experimental DOS obtained by Gurlu, Zandvliet, and Poelsema [1, Figure 3], there is agreement as concerns the gross structure of the surface DOS. However, the experiment does not fully resolve the fine structure. In particular, the experimental structure at -0.5 eV probably consists of two peaks, as indicated by a small shoulder on the low energy side, according to our peaks at -0.4 eV and -0.3 eV. Moreover, our DOS peaks at -0.9 eV and -0.8 eV are present in the experiment at slightly different energies. This may be due to the underestimation of the band gap in our calculation or due to the uncertainties of the experimental DOS coming along with the numerical evaluation of the differential conductivity. For the unoccupied bands, differences between theory and experiment appear to be larger at first glance. However, our four surface states can be identified in the experimental DOS, only their relative weights differ. The first peak at 0.2 eV seems to correspond to a tiny shoulder right above the Fermi level, which has not been discussed by Gurlu, Zandvliet, and Poelsema. The peaks at 0.4 eV, 0.6 eV, and 0.7 eV on the other hand perfectly agree with experiment.

We finally comment on the interpretation of the experimental surface DOS. As concerns the σ -type bonding and antibonding dimer bands our findings are fully in line with the conclusions of Gurlu, Zandvliet, and Poelsema. The same is true for the highest occupied and lowest un-

occupied surface state, except that we find a two peak structure. For the remaining surface bands (at -0.8 eV and 0.6 eV in our data) the interpretation of the experiment is difficult. The authors therefore have to speculate about the origin of these states, particularly due to a lack of state-of-the-art electronic structure data for comparison [1]. Our results clearly show that all occupied surface states, except for the σ -type dimer states, originate from the dangling D_{up} bonds, therefore giving rise to almost pure D_{up} surface bands. Similarly, the three lowest unoccupied surface states trace back to the dangling D_{down} bonds, forming likewise pure D_{down} surface bands.

In conclusion, we have investigated the surface electronic structure of the $c(4 \times 2)$ reconstructed Ge(001) surface by means of band structure calculations within density functional theory. Taking into account the details of the structural relaxation, we have discussed the surface density of states and established comprehensive insight

into the various surface states. In particular, it is possible to attribute each state to either the Ge dimer bonds or the dangling up/down bonds of the surface atoms. Our band structure results agree well with the local density of states obtained by spatially resolved scanning tunneling spectroscopy. As a consequence, we are able to clarify the interpretation of the experimental data for the $c(4 \times 2)$ reconstructed Ge(001) surface. We expect that similar studies can shed new light on related semiconductor surfaces, like Si(001) or GaAs(001).

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